(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 239 123**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **87104587.8**

(22) Date of filing: **27.03.87**

(51) Int. Cl.⁴: **G 11 B 5/71**, C 08 G 65/32, C 08 L 71/02

(30) Priority: **27.03.86 IT 1991086**

(43) Date of publication of application: **30.09.87**
Bulletin 87/40

(84) Designated Contracting States: **AT BE DE ES FR GB IT NL SE**

(71) Applicant: **AUSIMONT S.p.A., 31, Foro Buonaparte, I-20121 Milano (IT)**

(72) Inventor: **Scarati, Mario Alberto, 20, Via Bronzino, I-20133 Milan (IT)**
Inventor: **Caporiccio, Gerardo, 13, Via E. Filiberto, I-20149 Milan (IT)**

(74) Representative: **Barz, Peter, Dr. et al, Patentanwälte Dipl.-Ing. G. Dannenberg Dr. P. Weinhold, Dr. D. Gudel Dipl.-Ing. S. Schubert, Dr. P. Barz Siegfriedstrasse 8, D-8000 München 40 (DE)**

(54) Perfluoropolyether inner lubricants for magnetic recording media.

(57) Difunctional perfluoropolyether compounds having polar or non-polar hydrogenated end groups, suitable for being used as inner lubricants in the chemical formulation of the active layer of magnetic recording media, are characterized by a solubility in methyl ethyl ketone at 20 °C ranging from 0.5 to 2% by weight.

EP 0 239 123 A2

PERFLUOROPOLYETHER INNER LUBRICANTS FOR MAGNETIC RECORDING MEDIA

The invention relates to the lubrication of the magnetic recording media (records or tapes) based on magnetic pigments by means of inner-type lubricants, consisting of compounds having a perfluoropolyethereal structure, having hydrogenated end groups, having a critical solubility, as defined hereinafter, in the polymeric matrix constituting the magnetic layer.

As is known, within the class of the magnetic media based on particles or pigments, the recording magnetic medium comprises a layer of magnetic material spread on a rigid or flexible substrate.

Said layer is composed of magnetic oxide particles and/or metal particles dispersed in a thermoplastic or thermosetting polymeric binder, the base of which can be a polyvinyl, polyurethane, epoxy or phenolepoxy material, or proper mixtures thereof.

Other compounds are present in these formulation, their task being that of promoting the wettability and the dispersion of the magnetic pigments, or that of acting as lubricants to facilitate the sliding of the reading head on the magnetic medium.

These compounds are generally referred to as "inner lubricants". The inner lubricant must possess a few typical characteristics; it must be partially soluble in the resin and compatible with same, but it has not to act as a swelling agent

or as a plasticizer on the resin, as in such case it would very adversely affect the compactness and the mechanical characteristics thereof, in particular the resistance to wear.

The inner lubricant's mechanism of action, therefore, proves to be a slow and controlled migration through the micropores of the magnetic layer towards the surface, under the action of the temperature in the point of contact with the reading/writing heads and of the pressure resulting from this contact.

The materials generally utilized as inner lubricants are esters of fatty acids, fatty acids with a ramified or non-ramified chain, or mixtures thereof.

In spite of securing satisfactory performances and an increase in the life and abrasion resistance of the magnetic medium, these substances, utilized at present in all the flexible magnetic media, result to be little stable in the long run and are sensible to oxidation.

It is known that better results with regard to friction and to duration are obtainable by using surface perfluoropolyethereal lubricants, owing to their higher thermal and chemical stability and to their better lubricating properties.

While at the beginning neutral perfluoropolyethers were utilized as surface lubricants, improvements were achieved later according to what is disclosed in US patents Nos. 4,263,556 and 4,267,238, by introducing end groups of polar and reactive nature into the perfluoropolyether chain.

This method, generally utilized in the field of the magnetic media of a more advanced technology, such as the rigid discs for computers, comprises a step, subsequent to the preparation of the medium, in which a thin lubricant film is applicated onto the surface in the form of a dilute solution.

In order to avoid this post-treatment with the lubricant, which involves considerable practical complications and a remarkable increase in the production costs, there are utilized inner lubricants of the above-mentioned type, which are directly introduced into the resin composition utilized to form the magnetic layer. This process is possible only in the case of flexible magnetic recording media.

However, the tested compounds, of the type of fatty acid esters, exhibited the abovesaid drawbacks.

Thus, there was the increasing need to have available an inner lubricant, stable to heat and to chemical agents, resistant to oxidation and capable of securing the obtainment of magnetic media exhibiting higher performances than the ones attainable with the known hydrogenated inner lubricants, in particular as regards the use over an extended period of time.

On the other hand, neutral perfluoropolyethers are not utilizable as inner lubricants, due to their low compatibility with and low solubility in the hydrogenated resins utilized as binders.

Such low solubility results in a quick and uncontrolled surface migration of the lubricant, with consequent phenomena of sticking and formation of stains and deposits on the surface.

Furthermore, perfluoropolyether compounds with functional end groups of various type, having a too high solubility in the polymeric matrix used as a binder, are not utilizable because, acting as plasticizers, they cause a substantial worsening of the mechanical characteristics of the magnetic layer.

It has now surprsisingly been found that particular types of perfluoropolyethers having the two, polar or non-polar, end groups hydrogenated, and liquid at a temperature of 25°C, when used as inner lubricants, lead to considerable improvements in the performances of the flexible magnetic media obtained using such lubricant.

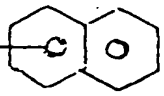
Object of the present invention is therefore the use of inner lubricants in resin compositions for paints for magnetic recording media of the flexible type, said lubricants being bifunctional perfluoropolyether compounds, liquid at a temperature of 25°C, having hydrogenated polar or non-polar end groups, having an average molecular weight of the perfluorooxyalkylene chain of at least 1,000, having a solubility at 20°C in methyl ethyl ketone ranging from 0.05% by weight to 2% by weight, extremes included.

Another object of the present invention are resin compositions containing from 0.5 to 3% by weight of the inner lubricants described above.

The presence of hydrogenated end groups, of the polar or non-polar type, in combination with a sequence of perfluorooxyalkylene units of a suitable length, ensures a partial compatibility with the resin, as is necessary in order to obtain a constant and controlled migration of the lubricant to the surface. In practice, the suitability of the perfluoropolyether compound can be ascertained on the basis of its solubility in methyl-ethyl-ketone at 20°C: it must range in fact from 0.05 to 2% by weight.

The hydrogenated end groups which usually impart the proper solubility degree to the product, are the ones having for example hydroxy, ester, aromatic, heterocyclic end groups which contain oxygen.

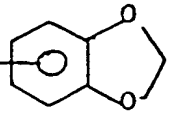
In particular, the lubricants of the invention have end groups T and T' preferably selected from:

a) $-CH_2O$  ;

b) $-CH_2O-(CH_2CH_2O)_zH$, where z is an integer from 1 to 3;

c) $-CH_2O$  ;

d) -COOR, where R is an alkyl radical with 2 to 12 carbon atoms;

e) $-CH_2O$ 

Suitable perfluoropolyether compounds according to the invention are in particular those belonging to the following classes:

(I) $TO(CF_2CR_2O)_n(CF_2O)_m-T'$;

(II) $TO(CF_2CF_2O)_g(CF_2O)_h\left(CFCF_2O\right)_p\left(CFO\right)_q T'$; with CF_3 substituents

(III) $TO(CF_2CF_2CF_2O)_s T'$;

(IV) $T(OCF_2CF_2CH_2)_t OR_fO (CH_2CF_2CF_2O)_t T'$;

(V) $TO(CF_2CF_2O)_r T'$;

(VI) $T(OCF_2CF)_u OR_fO (CF-CF_2O)_u T'$; with CF_3 substituents

wherein:

T and T', equal or different from each other, are hydrogenated end groups for instance of the kind defined hereinabove;

indexes n, m, g, h, p, q, s, t, r, u are integers selected in such manner, that the perfluoropolyether chain has a mean molecular weight of at least 1 000, preferably from 1 300 to 4 500, and in any case such that the perfluoropolyether is liquid at 25°C;

R_f is a fluoroalkylene radical preferably containing 1 to 12 carbon atoms; the perfluoro-oxyalkylene units being statistically distributed along the chain.

Among the compounds described as suited to be used as inner lubricants according to the invention, the preferred are the ones having the perfluoro-oxyalkylene chain of type (I) with

both end groups of type a) or of type b) indicated above.

The perfluoropolyethers utilizable for the present invention are preparable as follows:

- the ones of class (I) according to the processes described in US patent No. 3,242,218;
- the ones of class (II) according to US patent No. 3,665,041;
- the ones of classes (III) and (IV) according to European patent publication EP 148,432;
- the ones of class (V) according to US patent No. 4,523,039;
- the ones of class (VI) according to European patent publication EP 148,432.

The functional end groups suitable for the present invention can be introduced according to the methods described in US patent No. 3,310,874 and in European patent publication EP 165,649 and EP 165,650.

In the case of classes (II), (III) and (V), in which the starting perfluoropolyethers have only one functional end group, it is possible to pass to the corresponding difunctionalized product through the process described in Italian patent application No. 22920 A/85.

As mentioned above, the essential feature of an inner lubricant is that of having a critical solubility, limited in a narrow range, in the resin composition in which it is utilized.

It has been ascertained that the products having such feature possess also a critical solubility, limited to an exactly defined range (from 0.05% to 2% by weight at 20°C), in solvents such as tetrahydrofuran (THF), methylethylketone (MEK), isopropanol (iPrOH), these being hydrogenated solvents which, as is known, are used in the resin compositions utilized to form the magnetic layer.

For illustrative purposes, the solubilities of a few perfluoropolyether compounds of the invention in the above-said solvents are indicated hereinafter.

Furthermore, the data concerning the solubility of a perfluoropolyether compound unsuitable for the purposes of the invention and utilized in the following examples as a comparison are reported too.

T A B L E I

Solubility (% by weight) at 20°C

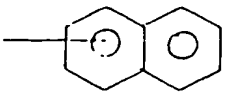
Substance	THF	MEK	iPrOH
A	0.10	0.15	0.15
B	0.12	0.17	0.18
C	0.12	0.14	0.16
D (comparative)	0.02	0.03	0.03

The substances indicated with A, B, C and D are respectively:

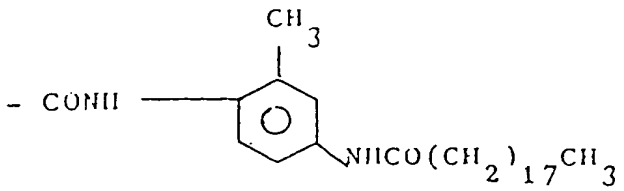
A : perfluoropolyether of class (I) having a mean molecular weight

of the perfluoropolyether chain equal to 2 000 and both end groups of formula: $-CH_2OCH_2CH_2OH$;

B : perfluoropolyether of class (I) having a mean molecular weight of the perfluoropolyether chain equal to 2 000 and both end groups of formula: $-CH_2OCH_2CH_2OCH_2CH_2OH$;

C : perfluoropolyether of class (I) having a mean molecular weight of the perfluoropolyether chain equal to 2 000 and both end groups of formula : CH_2O 

D : perfluoropolyether of class (I) having a mean molecular weight of the perfluoropolyether chain equal to 2 000 and both end groups of formula:



The fluorinated inner lubricants of the invention are utilizable in the resin compositions which form the magnetic layer in amounts ranging from 0.5 to 3% by weight.

The following examples are only illustrative of the invention and are not to be construed as a limitation thereof.

EXAMPLE 1

Preparation of video tapes

Video tapes based on polyurethane/epoxy resins were prepared, using the following composition (parts by weight):

a) Pigment (magnetic)

ferrite BAYFERROX ® AC type 5127 M 76.0

b) Resins

phenolepoxy resin UNION CARBIDE UCAR ® type PKHH 4.82

polyurethane prepolymer GOODRICH ESTANE ® 5701 F1 14.46

c) Crosslinking agent

DESMODUR ® R of Bayer (isocyanate crosslinking agent) 1.02

d) Dispersant

GAFAC ® RM 710 (phosphoric acid ester) 3.0

e) Inner lubricant :

in variable concentrations from 1 to 3% by weight on the total of the above-specified composition, selected from compounds A, B, C of the invention and comparative compound D described hereinbefore and isocetyl-stearate (ICS) (a further comparative compound, utilized in the art as an inner lubricant).

The paint was prepared according to known methods by preparing a suspension of the pigment in the solvent (MEK/THF = 30/70) with the aid of the dispersant; the resins dissolved in an analogous solvent, as well as the crosslinking agent and the inner lubricants of the invention were subsequently added. The

paint contained 50% by weight of solvent and 50% by weight of the other components a) through e) indicated hereinabove. A dispersion in grinding microball mill was then carried out, followed by filtration of the non-dispersed oxide aggregates.

The resulting magnetic paint was spread by means of the reverse roll coating technique onto 6" polyethylene terephthalate tapes having a thickness of 50 microns; the magnetic layer was subjected to orientation of the pigment and to calendering.

The tapes so obtained were cut to size 1/2" and wound in standard video cassettes VHS.

EXAMPLE 2

"Still frame life" test

On the tapes prepared according to example 1, a signal consisting of color bars was recorded, and the signal was reproduced maintaining the tape in the still-frame operation in which the tape stand still and the heads, mounted on the head-holding drum in rotation, went on sliding on the same path.

The life in this test is indicative of the abrasion resistance of the magnetic coating, and therefore it is strongly influenced by the presence of lubricants and by their efficacy.

The results are reported in Table 2.

Table 2

Inner lubricant (% by weight)	Still frame life (minutes)
A (1%)	85
A (3%)	90
C (1%)	75
TCS (1%)	55
TCS (3%)	50

EXAMPLE 3

The video tapes prepared according to the method of example 1 were subjected to friction coefficient tests in accordance with standards ASTM D 1894-73 and DIN 53375.

The utilized apparatus consisted of a platform of one of the two materials forming the kinematic couple, in the present case a chromium sheet; the other component of the kinematic couple consisted of a loaded slide covered by the tape stretched on it.

The static and the dynamic COF (friction coefficient) are reported in Table 3.

Table 3

Inner lubricant (% by weight)	Static COF	Dynamic COF
A (1%)	0.45	0.42
A (2%)	0.45	0.44
B (1%)	0.32	0.28
C (1%)	0.50	0.43

Table (continuation)

Inner Lubricant (% by weight)	Static COF	Dynamic COF
D (1%)	0.65	0.61
ICS (1%)	0.70	0.68
ICS (3%)	0.80	0.79

EXAMPLE 4

The tapes prepared according to example 1 were subjected to the abrasion test conforming to the method developed by the Fulmer Laboratories.

In this test, the abrasivity sensor consisted of a small ceramic cylinder onto which a thin metal layer had been deposited which was abraded by the tape sliding on it.

Said abrasion caused a change in the electric resistance of the thin-film sensor, so giving rise to a signal which, properly processed and calculated as a function of the time, permitted to determine the abrasivity value of the tape, such value being useful to determine the wear of the heads caused by the tape sliding thereon.

The results are expressed in arbitrary units (variation of the electric resistance of the sensor per unit of length of the tape, in particular for an average of 10 passages on 400 ft of tape) in Table 4.

Table 4

Inner lubricant (% by weight)		Abrasivity
A	(1%)	84
A	(3%)	90
D	(1%)	130
ICS	(1%)	156
ICS	(3%)	321
none		438

CLAIMS:

1. The use of bifunctional perfluoropolyether compounds, liquid at a temperature of 25°C, having hydrogenated polar or non-polar end groups, having an average molecular weight of the perfluorooxyalkylene chain of at least 1 000 and having a solubility at 20°C in methyl ethyl ketone ranging from 0.05 to 2% by weight, extremes included, as inner lubricants in resin compositions for paints for magnetic recording media of the flexible type.

2. The use according to claim 1, wherein the molecular weight of the perfluoropolyether chain ranges from 1 800 to 4 500.

3. The use according to claim 1 or 2, wherein the difunctional perfluoropolyether compounds are selected from:

(I) $TO(CF_2CF_2O)_n(CF_2O)_m-T'$;

(II) $TO(CF_2CF_2O)_g(CF_2O)_h(\underset{\displaystyle CF_3}{\underset{|}{CFCF_2O}})_p(\underset{\displaystyle CF_3}{\underset{|}{CFO}})_q T'$;

(III) $TO(CH_2CF_2CF_2O)_s T'$;

(IV) $T(OCF_2CF_2CH_2)_t OR_fO (CH_2CF_2CF_2O)_t T'$;

(V) $TO(CF_2CF_2O)_r T'$;

(VI) $T(OCF\text{-}\underset{\displaystyle CF_3}{\underset{|}{CF}})_u OR_fO (\underset{\displaystyle CF_3}{\underset{|}{CFCF_2O}})_u T'$;

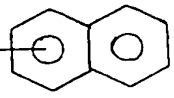
wherein:

T and T', equal or different from each other, are

hydrogenated end groups as defined above;
indices n, m, g, h, p, q, s, t, r, u are integers;
Rf is a fluoroalkylene radical;
the perfluorooxyalkylene units being statistically distributed along the chain.

4. The use according to claim 3, wherein end groups T and T' are hydroxy, ester, aromatic or heterocyclic groups containing oxygen.

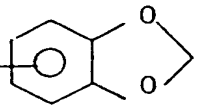
5. The use according to claim 3, wherein end groups T and T' are selected from:

a) $-CH_2O$  ;

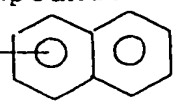
b) $-CH_2O-(CH_2CH_2O)_zH$, where z is an integer from 1 to 3;

c) $-CH_2O$  ;

d) -COOR, where R is an alkyl group with 2 to 12 carbon atoms;

e) $-CH_2O$  .

6. The use according to claim 3, wherein the difunctional perfluoropolyether compounds have the formula (I), wherein T and T' are $-CH_2O(CH_2CH_2O)_z$ with z being 1 or 2.

7. The use according to claim 4, wherein the difunctional perfluoropolyether compounds have the formula (I), wherein A and A' are $-CH_2O$  .

8. Resin compositions containing from 0.5 to 3% by weight of an inner lubricant as defined in any one of claims 1 to 7.